(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 199 436 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 86301444.5

(22) Date of filing: 28.02.86

(51) Int. Cl.[4]: C 08 F 2/38

(30) Priority: 01.03.85 US 707367
27.01.86 US 821321

(43) Date of publication of application:
29.10.86 Bulletin 86/44

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY
1007 Market Street
Wilmington Delaware 19898(US)

(72) Inventor: Melby, Lester Russell
2204 Graemar Road Hillendale
Wilmington Delaware 19809(US)

(72) Inventor: Janowicz, Andrew Henry
120 Birch Knoll Road
Wilmington Delaware 19810(US)

(72) Inventor: Ittel, Steven Dale
2802 Landon Drive Chalfonte
Wilmington Delaware 19810(US)

(74) Representative: Jones, Alan John et al,
CARPMAELS & RANSFORD 43 Bloomsbury Square
London, WC1A 2RA(GB)

(54) **Cobalt(II) chelates as chain transfer agents in free radical polymerizations.**

(57) Free radical polymerization processes employing cobalt (II) chelates of vicinal iminohydroxyimino compounds, dihydroxyimino compounds, diazadihydroxyiminodialkyldecadienes and diazadihydroxyiminodialkylundecadienes as catalytic chain transfer agents for controlling the molecular weight of the homopolymers and copolymers produced.

TITLE

Cobalt(II) Chelates As Chain Transfer Agents In Free Radical Polymerizations

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to free radical polymerization processes employing cobalt(II) chelates of vicinal iminohydroxyimino compounds, dihydroxyimino compounds, diazadihydroxyiminodialkyldecadienes and diazadihydroxyiminodialkylundecadienes as catalytic chain transfer agents for controlling the molecular weight of the homopolymers and copolymers produced.

Background

In any polymerization process it is necessary to be able to control the molecular weight of the polymer produced so that it may be fitted to a particular use or need. For example, in unperturbed polymerization systems which fundamentally tend to produce high molecular weight polymers, it may be desirable or necessary to limit the molecular weight of the polymers produced, and this must be done in a predictable and controllable fashion. Such molecular weight limitation may be desirable or necessary in the preparation of polymer solutions for use in paints and finishes which require high solids contents to assure reduced solvent emission during application, and yet which require low viscosity to facilitate ready application.

In free radical polymerizations there are several conventional means of effecting such molecular

weight limitation, but all have notable disadvantages. These include:

(1) The use of a high initiator/monomer ratio, but this is costly in terms of initiator consumption.

(2) Polymerizing at high temperatures, for example, about 150°C, which is undesirably energy intensive.

(3) Adding stoichiometric amounts of thiol chain transfer agents to the polymerizing system, but the attendant incorporation of sulfur-containing agents into the polymer renders it less durable than is desired.

(4) Odor problems associated with the use of sulfur-containing chain transfer agents.

Catalytic chain transfer to the monomer as a means of controlling molecular weight in the radical polymerization of methyl methacrylate and styrene in the presence of cobalt(II) porphyrin complexes is known in the art. N. S. Enikolopyan et al., J. Polym. Sci., Polym. Chem. Ed., Vol. 19, 879 (1981), describe the kinetics and the molecular weight control achieved in the free radical polymerization of methyl methacrylate in the presence of a cobalt complex of hematoporphyrin tetramethyl ether. This use of this cobalt complex is also discussed by B. R. Smirnov et al. in Vysokomol. soyed., A23, No. 5, 1042 (1981) and by B. R. Smirnov et al. in Dokl. Akad. Nauk SSSR, 253, 891 (1980). In a similar study, B. R. Smirnov et al., Dokl. Akad. Nauk SSSR, 254, 127 (1980), describe studies carried out with hematoporphyrin tetramethyl ester. The authors conclude that only the combination of cobalt with a tetrapyrrole porphyrin ligand apparently permits the realization of catalysis of chain transfer to the monomer, and that it has been ruled out that analogous phenomena will be

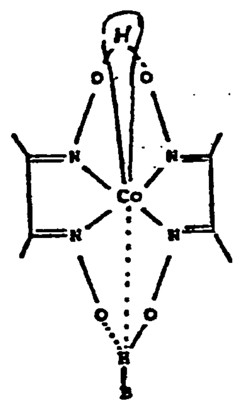
discovered during the investigation of complexes similar in spatial and electronic structure to the porphyrins, such as phthalocyanines, corrins, cobaloximes, etc. B. R. Smirnov et al., Vysokomol. soyed., A23, No. 11, 2588 (1981), describe the catalytic chain transfer observed in the radical polymerization of styrene in the presence of a cobalt complex of hematoporphyrin IX tetramethyl ester.

D. E. Pashchenko et al., Dokl. Akad. Nauk SSSR, 265, 889 (1982), describe chain transfer studies with cobalt porphyrins in the polymerization of methyl methacrylate. Regarding this paper, it is not understood what is meant by "cobalt complexes of porphyrins and cobaloximes" since there is no further mention of "cobaloximes" in the English language version of the paper; moreover, the term "cobaloximes" does not appear in the original Russian text, but rather the term "cobalamines", which are vitamin B12-related structures similar to the porphyrin structures disclosed in this paper and in the other publications cited above.

Although the use of the porphyrin complexes circumvents many of the problems associated with the aforesaid conventional commercial processes, the complexes impart too much color to the final product, rendering it useless or less desirable in many applications, such as in certain paints and finishes. Moreover, the cost of the porphyrin complex is rather high.

A. F. Burczyk et al., J. Polym. Sci., Polym. Chem. Ed., Vol. 22, 3255 (1984), disclose that cobaloximes, that is, bisdimethylgloximatocobalt complexes, are often used as analogs of cobalt porphyrins in research studies, and they further disclose the use of cobaloxime, synthesized from Co(II) acetate and dimethylglyoxime, as a relatively cheap

chain transfer agent in the free radical polymerization of methyl methacrylate. The cobaloxime of Burczyk et al. is shown on page 3256 as being of the formula



wherein B is a coordinating base ligand, such as triphenylphosphine. Similar disclosures are made by A. F. Burczyk in a thesis to the University of Waterloo, Waterloo, Ontario, 1984.

Carlson et al., U.S. 4,526,945, also disclose the use of cobalt(II) dimethylgloxime and similar cobalt(II) dioxime pyridine complexes such as those derived from 2,3-butanedione, 2,3-hexanedione, 2,4-heptanedione, 2,5-dimethyl-3,4-hexanedione, 3-methyl-2,4-hexanedione, 1,2-cyclohexanedione, 3-phenyl-2,4-pentanedione, 2-naphthylglyoxal, camphoroquinone, 4-chloro-1,2-benzoquinone, 1,2-napthoquinone, 3,7-dimethyl-1,2-napthoquinone, 3-chloro-1,2-napthoquinone or substituted 1,2-anthraquinones as molecular weight control agents in homogeneous polymerizations.

H. C. Rai et al., Indian Journal of Chemistry, Vol. 18A, 242 (1979), describe the preparation of the cobalt chelates of cobalt(II) with 4,7-diaza-2,9-dihydroxyimino-3,8-dimethyldeca-3,7-diene and cobalt(II) with 4,8-diaza-2,1-dihydroxyimino-3,9-dimethylundeca-3,8-diene. There is no disclosure as to the use of these compounds as catalytic chain transfer agents. E.

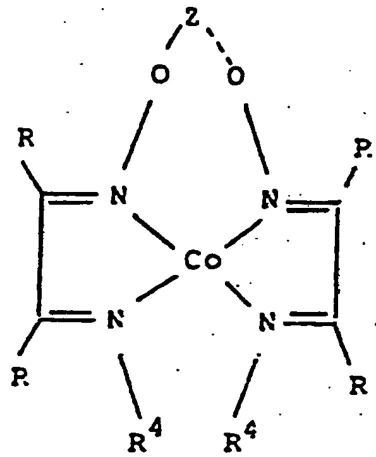
Uhlig et al., Z. anorg. allg. Chem., 343, 299 (1966), describe the preparation of the ligands 4,7-diaza-2,9-dihydroxyimino-3,8-dimethyldeca-3,7-diene and 4,8-diaza-2,10-dihydroxyimino-3,9-dimethylundeca-3,8-diene compounds. G. N. Schrauzer, Inorg. Syn., 11, 62, 64 (1968), describes the preparation of diaqua bis(2,3-dihydroxyiminobutanato)Co(II). A. Bakac et al., J. Am. Chem. Soc., 106, 5197 (1984), describe the preparation of Co(II)(2,3-dioxyiminobutane-BF_2)$_2$(H_2O)$_2$.

It is an object of this invention to provide cobalt(II) chelates of vicinal iminohydroxyimino compounds, dihydroxyimino compounds, diazadihydroxyiminodialkyldecadienes and diazadihydroxyiminodialkylundecadienes which operate as highly efficient catalytic chain transfer agents for controlling homopolymer and copolymer molecular weights, while imparting very little, if any, color to the final products, making them more useful in many applications, such as in paints and finishes.

Another object is to provide such a process which proceeds at modest temperatures, for example, about 65 to about 110°C, with limited amounts of initiator and in the absence of stoichiometrically-reacting chain transfer agents. These and other objects will become apparent hereinafter.

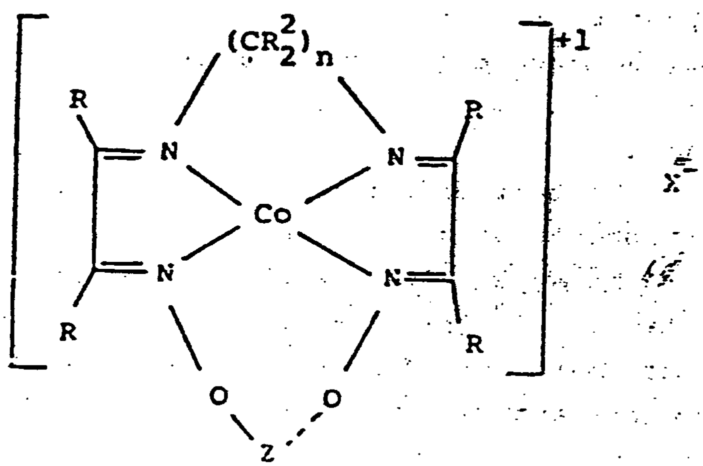
SUMMARY OF THE INVENTION

The present invention provides improved processes for controlling the molecular weight of homopolymers and copolymers produced in free radical polymerizations, the improvement characterized in that molecular weight control is effected by means of a cobalt chelate chain transfer agent of the formula

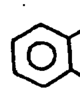
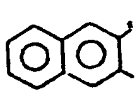


(III)

or



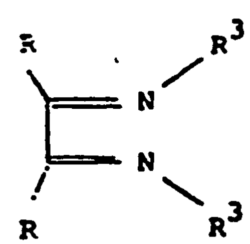
(IV)

wherein each R, independently, is phenyl or C_1 to C_{12} alkyl wherein each α-carbon atom contains two hydrogen atoms, or R and R on adjacent carbon atoms, taken together, is C_5 to C_8 cycloalkylene, unsubstituted in the α-positions, -CH=CH-CH=CH-, CH=CH-, or CH=CH-; R^2 is H or C_xH_{2x+1} wherein x is

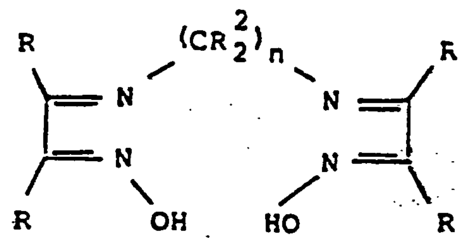
1 to 12; each R^4, independently, is H or C_xH_{2x+1} wherein X is 1 to 12, or both R^4 groups taken together is $-O-Z---O-$; n is 2 or 3; Z is BF_2, BCl_2, BBr_2 or BR^2_2; and X^- is NO_3^-, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, SbF_6^- or R^1COO^- wherein R^1 is C_1 to C_{12} alkyl.

DETAILED DESCRIPTION OF THE INVENTION

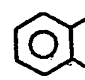
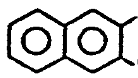
This invention resides in polymerization processes employing cobalt(II) chelates as catalytic chain transfer agents for controlling the molecular weights of the homopolymers and copolymers produced. The cobalt chelates consist of cobalt(II) coordinated to the following ligands: vicinal iminohydroxyimino and dihydroxyimino compounds (I), and diazadihydroxyiminodialkyldecadienes and -undecadienes (II). By "ligand", as the term is used herein, is meant any atom, radical or molecule which can bind to a characteristic or central element of a complex. The structures of the aforesaid ligands are given below.

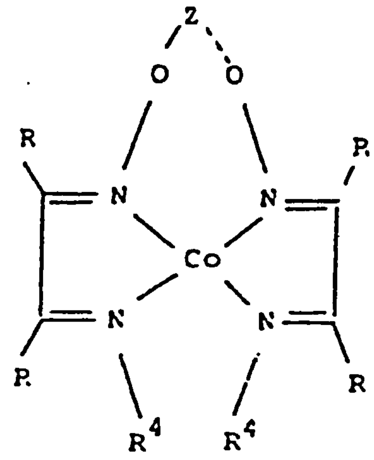


(I)

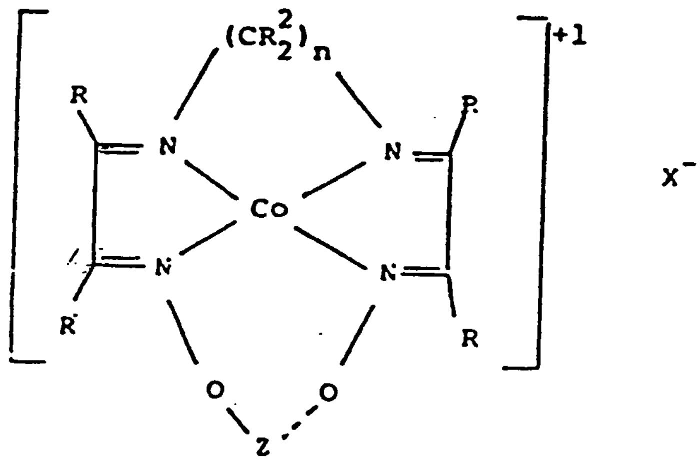


(II)

In the aforesaid formulas each R, independently, is phenyl or C_1 to C_{12} alkyl wherein each α-carbon atom contains two hydrogen atoms, that is, is unsubstituted, or R and R on adjacent carbon atoms, taken together, is C_5 to C_8 cycloalkylene, unsubstituted in the α-positions, -CH=CH-CH=CH-, CH=CH-, or CH=CH-; R^2 is H or C_xH_{2x+1} wherein x is 1 to 12; each R^3, independently, is H, C_xH_{2x+1} wherein x is 1 to 12, or OH, with at least one being OH; and n is 2 or 3. The corresponding structures for the cobalt chelates of these ligands are given below. More specifically, the corresponding cobalt chelate of structure I is III, and the corresponding cobalt chelate of structure II is IV.



(III)



(IV)

In formulas III and IV, R, R^2 and n are as defined above; each R^4, independently, is H or C_xH_{2x+1} wherein X is 1 to 12, or both R^4 groups taken together is -O-Z---O-; Z is BF_2, BCl_2, BBr_2 or BR^2_2; and X^- is NO_3^-,

Cl^-, Br^-, I^-, BF_4^-, PF_6^-, SbF_6^- or R^1COO^- wherein R^1 is C_1 to C_{12} alkyl. The cobalt chelates of the above formulas may also, but need not, be coordinated with additional ligands derived from materials present in the reaction medium such as water, alcohols or ketones.

Preparation of iminohydroxyimino compounds, dihydroxyimino compounds, diazadihydroxyiminodialkyldecadienes and diazadihydroxyiminodialkylundecadienes, and cobalt chelate catalytic chain transfer agents of Formulas III and IV from such iminohydroxyimino compounds, dihydroxyimino compounds, diazadihydroxyiminodialkyldecadienes and diazadihydroxyiminodialkylundecadienes can be accomplished using methods known in the art, such as those set forth in H.C. Rai et al., Indian Journal of Chemistry, Vol. 18A, 242 (1979), E. Uhlig et al., Z. anorg. allg. Chem., 343, 299 (1966), G. N. Schrauzer, Inorg. Syn., 11, 62 (1968), and A. Bakac et al., J. Am. Chem. Soc., 106, 5197 (1984).

The preferred chain transfer agents herein are cobalt(II) salts coordinated to the ligands of Formula I wherein both R^4 groups taken together is -O-Z---O-. Most preferred are Co(II)(2,3-dioxyiminobutane-BF_2)$_2$, Co(II)(1,2-dioxyiminocyclohexane-BF_2)$_2$, and Co(II)(1,2-diphenyl-1,2-dioxyiminoethane-BF_2)$_2$.

The polymerization can be carried out either in the absence of a polymerization medium, as a bulk polymerization, or alternatively, in the presence of a polymerization medium, as a solution, suspension or emulsion polymerization.

Many common organic solvents are suitable as solution polymerization media. These include aromatic hydrocarbons, such as benzene, toluene and the xylenes; ethers, such as tetrahydrofuran, diethyl ether and the commonly available ethylene glycol and polyethylene glycol monoalkyl and dialkyl ethers, including the

Cellosolves® and Carbitols®; alkyl esters of acetic, propionic and butyric acids; mixed ester-ethers, such as monoalkyl ether-monoalkanoate esters of ethylene glycol; and amides such as formamides and acid amides. In addition, ketones, such as acetone, butanone, pentanone and hexanone, are suitable, as are alcohols, such as methanol, ethanol, propanol and butanol. Water may be used as a solvent for water soluble monomers. In some instances, it may be advantageous to use mixtures of two or more solvents.

In emulsion and suspension polymerizations, the suitable medium is water in combination with any conventional suspending or emulsifying agent. Emulsifying agents can be anionic such as sodium dodecylsulfate or cationic such as hexadecyltrimethylammonium bromide. The suspending agent used in the reaction can be Acrysol A-3, a polyacrylic acid made by Rohm & Haas Company.

The bulk and solution polymerizations can be carried out at 50-150°C, with the preferred range 80-110°C. The emulsion and suspension polymerizations can be carried out at 25-90°C, with the preferred range 65-80°C.

Any of the known class of azo polymerization initiators is suitable provided it has solubility in the solvent, monomer mixture, or water, as the case may be, and has an appropriate half life at the temperature of polymerization. "Appropriate half life", as used herein, is a half life of about 1-4 hours. Typical of such initiators, but not restricted to them, are azocumene, 2,2′-azobis(isobutyronitrile), 2,2′-azobis-(2-methyl)butanenitrile, 4,4′-azobis(4-cyanovaleric acid), and 2-(t-butylazo)-2-cyanopropane. Other soluble non-azo initiators having an appropriate half life may

also be used, including, among others, benzoyl peroxide, lauroyl peroxide, persulfates, and molecular hydrogen.

The process of the invention can be carried out as either a batch or feed process. In either type of process the polymer is isolated by stripping off solvent and unreacted monomer or by precipitation with a nonsolvent. Alternatively, the polymer solution may be used as such if appropriate to its application.

The process of the invention can be carried out with monomers such as methacrylate; acrylate; acrylic acid; styrene; vinyl acetate; acrylonitrile; methacrylonitrile; vinyl halides of the formula $CH_2{=}CHX$, wherein X is Cl or F; vinylidene halides of the formula $CH_2{=}C(X)_2$, wherein each X is, independently, Cl or F; substituted butadienes of the formula $CH_2{=}C(R)C(R){=}CH_2$, wherein each R is, independently, H, C_1 to C_{10} alkyl, Cl or F; ethylenesulfonic acid derivatives of the formula $CH_2{=}CHSO_3X$, wherein X is Na, K, Li, $N(R)_4$, H, R, or $(CH_2)_nZ$, each R is, independently, C_1 to C_{10} alkyl, n is an integer from 1 to 10, Z is COOY, OH, $N(R)_2$, or SO_3Y, and Y is H, Li, Na, K or $N(R)_4$; acrylamide derivatives of the formula $CH_2{=}CHCON(R)_2$, wherein each R is, independently, H, C_1 to C_{10} alkyl, or $(CH_2)_nZ$, n is an integer from 1 to 10, Z is COOY, OH, $N(R)_2$, or SO_3Y and Y is H, Li, Na, K, or $N(R)_4$; methacrylamide derivatives of the formula $CH_2{=}C(CH_3)CON(R)_2$, wherein each R is, independently, H, C_1 to C_{10} alkyl or $(CH_2)_nZ$, n is an integer from 1 to 10, Z is COOY, OH, $N(R)_2$, SO_3Y, and Y is H, Li, Na, K, or $N(R)_4$; vinyl acetates of the formula $CH_2{=}CHOOCR$, wherein R is C_1 to C_{10} alkyl; and with any and all monomer mixtures thereof.

The bulk and solution polymerizations of the invention are carried out most effectively with styrene, methacrylate ester, and methacrylonitrile monomers. The suspension and emulsion polymerizations of the instant

invention are carried out most effectively with methacrylate ester momomers. Methacrylates which are useful in this invention include branched alkyl or n-alkyl esters of C_{1-12} alcohols and methacrylic acid, for example, methyl and ethyl methacrylate. Other monomers include, but are not restricted to, allyl, glycidyl, hydroxyalkyl (for example, hydroxyethyl and hydroxypropyl), allyloxyethyl, 2,4-hexadienyl (sorbyl) and dialkylaminoalkyl methacrylates.

To ensure maximum catalyst activity the polymerizations should be carried out in the substantial absence of oxygen under an inert atmosphere, such as nitrogen, argon or other non-oxidizing gas. "Deaeration", as the term is used herein, means the substantial removal of oxygen.

The invention is further described in the Examples set forth below. The polymerizations discussed therein were conducted substantially according to the following General Procedures, except where otherwise indicated. In the General Procedures and Examples, all parts are by weight, and all temperatures are given in degrees Celsius, unless otherwise stated. It should be noted that where values are less than 1000, molecular weight is difficult to determine with accuracy. Nevertheless, the decrease in molecular weight shown by these valves is an accurate reflection of molecular weight control.

GENERAL PROCEDURES

A. Solution Polymerization

In a nitrogen drybox, 21.4 ml (0.2 mol) of methyl methacrylate, which had been previously sparged with nitrogen and passed through a column of Woelm alumina (grade 1), was added to a 100 ml volumetric flask. To this was added the desired amount of cobalt catalyst and the volume was brought to 100 ml with distilled methanol.

To a 300 ml round bottom flask were added 0.062 g (2.5 x 10^{-4} mol) of 2,2-azobis(2-methyl)butanenitrile and the contents of the volumetric flask. The reaction mixture was then stirred to dissolve the 2,2'-azobis(2-methyl)butanenitrile and a gas chromatography (G.C.) sample was taken. The round bottom flask was capped with a water cooled condenser, brought out of the drybox and heated to reflux under nitrogen for six hours. The reaction mixture was then allowed to cool to room temperature and a second G.C sample was taken. The poly(methyl methacrylate) which was produced was isolated by removing solvent and monomer from the reaction mixture via a rotary evaporator. Gel permeation chromatography (GPC) was used to determine the average molecular weight ($\bar{M}_w$) and average molecular number ($\bar{M}_n$) of the polymer produced.

B. Suspension Polymerization

In a nitrogen dry box, 21.4 ml (0.2 mole) of methyl methacrylate, previously sparged with nitrogen and passed through a column of Woelm alumina (grade 1), 0.248 g (1.0 x 10^{-3} moles) of 2,2'-azobis[2-methyl]-butanenitrile and the desired amount of cobalt catalyst were placed into a 300 ml three neck round bottom flask equipped with a reflux condenser, septum and mechanical stirrer. The flask was brought out of the dry box and 60 ml of aqueous Acrysol A-3 [prepared by adding 75.5 g Acrysol A-3 to 1500 ml of water and degassed overnight] was added under an atmosphere of nitrogen. The flask was placed in a bath at 65°, the stirrer set at 400 rpm and the reaction allowed to proceed for two hours. A nitrogen atmosphere was maintained in the flask throughout the course of the reaction. After the allotted time, the reaction mixture was cooled to room temperature and the polymer collected by filtration.

The polymer was washed with water and dried. GPC was used to determine $\bar{M}_w$ and $\bar{M}_n$ of the polymer produced.

C. Emulsion Polymerization

In a nitrogen dry box, 21.4 ml (0.2 mole) of methyl methacrylate, previously sparged with nitrogen and passed through a column of Woelm alumina (grade 1), 0.374 g 4,4'azobis(4-cyanovaleric acid) and the desired amount of cobalt catalyst were placed into a 300 ml three neck round bottom flask equipped with a reflux condenser, septum, and mechanical stirrer. The flask was brought out of the dry box and 60 ml of 0.1M aqueous sodium dodecylsulfate (degassed) was added under an atmosphere of nitrogen. The flask was placed in a bath at 80°, the stirrer set at 400 rpm and the reaction allowed to proceed for four hours. A nitrogen atmosphere was maintained in the flask throughout the course of the reaction. After the allotted time, the reaction mixture was cooled to room temperature and the polymer precipitated by adding 150 ml of methanol. The polymer was collected by filtration, washed with methanol, washed with water, and air dried. GPC was used to determine $\bar{M}_w$ and $\bar{M}_n$ of the polymer produced.

EXAMPLES 1-3

A. Preparation of $[Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2]$

[DHIB=2,3 dioxyiminobutane]

The title compound was prepared by the method of A. Bakac et al., J. Am. Chem. Soc., 106, 5197-5202 (1984).

The suspension resulting from the addition of 10 ml of $BF_3.Et_2O$ to 2 g of $Co(OAc)_2.4H_2O$ and 1.9 g of 2,3-dihydroxyiminobutane in 150 ml of diethyl ether was stirred at room temperature overnight. The resultant solid $[Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2]$ was collected by filtration, placed into 250 ml of methanol and heated to reflux. The solid which did not dissolve was removed by

filtration (0.336 g). The remaining clear solution was placed in a freezer overnight. The crystallized product was recovered by filtration and dried (0.468 g). The remaining solution was reduced to a volume of 30 ml under vacuum and placed in a freezer (-25°C) overnight. An additional 0.101 g of product was recovered. The infrared spectra of the product exhibited bands at 3581 cm^{-1} (H_2O) and 1623 cm^{-1}, 950 cm^{-1} (BF).

B. The Use of $[Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2]$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Methyl Methacrylate

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
1	6.0×10^{-6} M	1470	2740	1.86
2	3.0×10^{-5} M	301	512	1.70
3	1.5×10^{-4} M	65	134	2.06

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 45,800, $\bar{M}w$ 122,000 and $\bar{M}w/\bar{M}n$ 2.66.

COMPARATIVE EXAMPLES 1-2

Attempted Use of $Co(II)(DHIB\text{-}H)_2(Ph_3P)$ and $Co(II)(DHIB\text{-}H)_2(C_5H_5N)$ as Catalytic Chain Transfer Agents in the Free Radical Solution Polymerization of Methyl Methacrylate

[PH_3P=Triphenyl phosphine]

The General Procedure for solution polymerization was followed using the indicated type and

amount of Co(II) catalyst. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
1	$Co(II)(DHIB)_2(Ph_3P)$ [6.0×10^{-6} M]	24,600	56,800	2.31

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
2	$Co(II)(DHIB)_2(C_5H_5N)$ [6.0×10^{-6} M]	39,500	82,100	2.08

EXAMPLES 4-6

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Methyl Acrylate

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst, methyl acrylate as monomer, 2,2'-azobis(isobutyronitrile) as initiator and methyl ethyl ketone as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
4	5×10^{-6} M	14,600	48,600	3.33
5	5×10^{-5} M	7,700	23,300	3.03
6	5×10^{-4} M	1,620	4,380	2.70

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 17,300, $\bar{M}w$ 56,500 and $\bar{M}w/\bar{M}n$ 3.27.

EXAMPLES 7-9

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Styrene

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst, styrene as monomer, 2,2'-azobis(isobutyronitrile) as initiator, and methyl ethyl ketone as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
7	5×10^{-6} M	5,210	14,600	2.80
8	5×10^{-5} M	734	1,580	2.15
9	5×10^{-4} M	45	122	2.71

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 21,700, $\bar{M}w$ 48,700 and $\bar{M}w/\bar{M}n$ 2.24.

EXAMPLES 10-12

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Methyl Methacrylate

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst, methyl methacrylate as monomer, 2,2'-azobis(isobutyronitrile) as initiator, and methyl ethyl ketone as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
10	5×10^{-6} M	1,020	2,110	2.07
11	5×10^{-5} M	90	219	2.43
12	5×10^{-4} M	48	59	1.20

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 37,100, $\bar{M}w$ 77,400 and $\bar{M}w/\bar{M}n$ 2.09.

EXAMPLES 13-15

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Methylacrylonitrile

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst, methacrylonitrile as monomer, 2,2′-azobis(isobutyronitrile) as initiator, and methyl ethyl ketone as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
13	5×10^{-6} M	341	492	1.44
14	5×10^{-5} M	71	113	1.59
15	5×10^{-4} M	56	93	1.66

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 1,140, $\bar{M}w$ 1,950 and $\bar{M}w/\bar{M}n$ 1.71.

EXAMPLES 16-18

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Isoprene

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst, isoprene as monomer, 2,2′-azobis(isobutyronitrile) as initiator, and methyl ethyl ketone as solvent. The cobalt catalyst was prepared according to the procedure described in

Examples 1-3. The molecular weight values were determined by nuclear magnetic resonance spectroscopy (NMR). The results are listed below.

Example	Catalyst	$\bar{M}w$
16	5×10^{-6} M	307
17	5×10^{-5} M	245
18	5×10^{-4} M	157

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}w$ 320.

EXAMPLES 19-21

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Vinyl Acetate

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst, vinyl acetate as monomer, 2,2'-azobis(isobutyronitrile) as initiator and methyl ethyl ketone as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
19	5×10^{-6} M	1,610	3,420	2.12
20	5×10^{-5} M	1,660	3,510	2.11
21	5×10^{-4} M	891	2,120	2.38

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 1,660, $\bar{M}w$ 3,579 and $\bar{M}w/\bar{M}n$ 2.16.

EXAMPLES 22-24

The Use of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Acrylonitrile

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as catalyst, acrylonitrile as monomer, 2,2'-azobis(isobutyronitrile) as initiator and methyl ethyl ketone as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. In the results listed below, [η] is the intrinsic viscosity which is proportional to molecular weight. The higher the value of [η], the higher the molecular weight. These values were determined by capillary viscometry (CV).

Example	Catalyst	[η] dl/g
22	5×10^{-6} M	0.5465
23	5×10^{-5} M	0.5410
24	5×10^{-4} M	0.4483

A colorless product was observed.

A repeat of the above experiment with no catalyst gave [η] dl/g 0.5533.

EXAMPLES 25

The Use of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of 2-Acrylamido-2-methylpropanesulfonic Acid

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as catalyst, 0.1 mole 2-acrylamido-2-methylpropanesulfonic acid as monomer, 1.0 x 10-3 moles of 2,2'-azobis(isobutyronitrile) as initiator and 100 ml of dimethylformamide as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The contents were

heated at 100°C under a nitrogen atmosphere for 90 minutes. The result, listed below, was determined by CV. [η] is defined in Examples 22-24.

Catalyst	[η] dl/g
5×10^{-4} M	0.1150

A colorless product was observed.

A repeat of the above experiment with no catalyst gave [η] dl/g 0.1525.

EXAMPLE 26

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of 2-Acrylamido-2-methylpropanesulfonic Acid

The General Procedure for solution polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst, 0.1 mole of 2-acrylamido-2-methylpropanesulfonic acid as monomer, 0.374 g of 4,4′-azobis(4-cyanovaleric acid) as the initiator and 100 ml of water as solvent. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The contents were heated at 100°C under a nitrogen atmosphere for 30 minutes. The result, listed below, was determined by CV. [η] is defined in Examples 22-24.

Catalyst	[η] dl/g
5×10^{-4} M	0.5832

A colorless product was observed.

A repeat of the above experiment with no catalyst gave [η] dl/g 0.8078.

EXAMPLE 27

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Solution Polymerization of Methacrylic Acid

Example 26 was repeated using methacrylic acid as monomer. The result is listed below.

Catalyst	[η] dl/g
5×10^{-4} M	0.0540

A colorless product was observed.

A repeat of the above experiment with no catalyst gave [η] dl/g 0.6862.

EXAMPLES 28-31

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Suspension Polymerization of Methyl Methacrylate

The General Procedure for suspension polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
28	0.25 ppm	109,000	668,000	6.10
29	2.50 ppm	41,400	150,000	3.62
30	25 ppm	1,050	2,990	2.83
31	100 ppm	307	1,650	5.38

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 110,000, $\bar{M}w$ 865,000 and $\bar{M}w/\bar{M}n$ 7.86.

EXAMPLES 32-34

The Use of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Emulsion Polymerization of Methyl Methacrylate

The General Procedure for emulsion polymerization was followed using the indicated amount of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as catalyst. The cobalt catalyst was prepared according to the procedure described in Examples 1-3.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
32	0.25 ppm	120,000	375,000	3.12
33	2.50 ppm	17,900	36,100	2.02
34	100 ppm	497	1,700	2.15

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 675,000, $\bar{M}w$ 3,694,000 and $\bar{M}w/\bar{M}n$ 5.48.

EXAMPLES 35-37

The Use of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Suspension Polymerization of Methyl Methacrylate

The General Procedure for suspension polymerization was followed using the indicated amount of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as catalyst and 0.025 g of initiator. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
35	0.25 ppm	244,000	1,788,000	7.31
36	2.5 ppm	41,500	332,000	8.00
37	25 ppm	727	1,450	1.99

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 481,000, $\bar{M}w$ 3,283,000 and $\bar{M}w/\bar{M}n$ 6.83.

EXAMPLES 38-40

The Use of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Emulsion Polymerization of Methyl Methacrylate

The General Procedure for emulsion polymerization was followed using the indicated amount of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as catalyst and 0.037 g of initiator. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
38	0.25 ppm	153,000	498,000	3.25
39	2.5 ppm	25,700	54,500	2.12
40	25 ppm	1,260	3,280	2.61

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 2,926,000, $\bar{M}w$ 7,002,000 and $\bar{M}w/\bar{M}n$ 2.39.

EXAMPLE 41

The Use of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Emulsion Polymerization of Methyl Methacrylate

The General Procedure for emulsion polymerization was followed using the indicated amount of $Co(II)(DHIB-BF_2)_2(H_2O)_2$ as catalyst and 0.0037 g of initiator. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The result is listed below.

Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
2.5 ppm	206,000	1,809,000	8.80

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 2,254,000, $\bar{M}w$ 4,736,000 and $\bar{M}w/\bar{M}n$ 2.10.

EXAMPLES 42-43

The Use of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer in the Free Radical Emulsion Polymerization of Methyl Methacrylate

The General Procedure for emulsion polymerization was followed using the indicated amount of $Co(II)(DHIB\text{-}BF_2)_2(H_2O)_2$ as catalyst and hexadecyltrimethylammonium bromide [0.025 M] as the cationic emulsifier. The cobalt catalyst was prepared according to the procedure described in Examples 1-3. The results are listed below.

Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
42	0.25 ppm	154,000	647,000	4.20
43	2.5 ppm	20,000	44,900	2.25

A colorless product was observed.

A repeat of the above experiment with no catalyst gave $\bar{M}n$ 368,000, $\bar{M}w$ 3,655,000 and $\bar{M}w/\bar{M}n$ 9.93.

EXAMPLE 44

A. Preparation of $Co(II)(DDE\text{-}H)_2(H_2O)_2$
[DDE = 1,2-diphenyl-1,2-dioxyiminoethane]

$Co(II)(DDE\text{-}H)_2(H_2O)_2$ was prepared by the method of G. N. Schrauzer, Inorg. Syn., 11, 64 (1968).

B. Preparation of $Co(II)(DDE\text{-}BF_2)_2(H_2O)_2$

In a dry box, $Co(II)(DDE\text{-}H)_2(H_2O)_2$ [5.0 g], $BF_3 \cdot O(C_2H_5)_2$ [10.0 ml] and 100 ml of $(C_2H_5)_2O$ were placed into a round bottom flask. The contents were stirred for 24 hours after which time the suspended solids were recovered by filtration and washed with diethyl ether. The recovered solids were dried under vacuum. Product yield = 5.56 g.

C. The Use of $Co(II)(DDE\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Emulsion Polymerization of Methyl Methacrylate

The General Procedure for emulsion polymerization was followed. The concentration of $Co(II)(DDE\text{-}BF_2)_2(H_2O)_2$ was 2.5 ppm. The resulting polymer had $\bar{M}n$ 171,000, $\bar{M}w$ 1,349,000 and $\bar{M}w/\bar{M}n$ 7.88. A colorless product was observed.

EXAMPLE 45

The Use of $Co(II)(DDE\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Suspension Polymerization of Methyl Methacrylate

The General Procedure for suspension polymerization was followed. The cobalt catalyst was prepared according to the procedures described in Example 44. The concentration of $Co(II)(DDE\text{-}BF_2)_2(H_2O)_2$ was 2.5 ppm. The resulting polymer had $\bar{M}n$ 7,420, $\bar{M}w$ 20,900 and $\bar{M}w/\bar{M}n$ 2.81. A colorless product was observed.

EXAMPLE 46

A. Preparation of $Co(II)(DC\text{-}H)_2(H_2O)_2$
[DC = 1,2-dioxyiminocyclohexane]

$Co(II)(DC\text{-}H)_2(H_2O)_2$ was prepared by the method of G. N. Schrauzer, Inorg. Syn., 11, 64 (1968).

B. Preparation of $Co(II)(DC\text{-}BF_2)_2(H_2O)_2$

In a dry box, $Co(II)(DC\text{-}H)_2(H_2O)_2$ [5.0 g], $BF_3 \cdot O(C_2H_5)_2$ [10.0 ml] and 100 ml of $(C_2H_5)_2O$ were placed into a round bottom flask. The contents were stirred for 24 hours after which time the suspended solids were recovered by filtration and washed with diethyl ether. The recovered solids were dried under vacuum. Product yield = 4.09 g.

C. The Use of $Co(II)(DC\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Emulsion Polymerization of Methyl Methacrylate

The General Procedure for emulsion polymerization was followed. The concentration of $Co(II)(DC\text{-}BF_2)_2(H_2O)_2$ was 2.5 ppm. The resulting polymer had $\bar{M}n$ 14,500, $\bar{M}w$ 31,500 and $\bar{M}w/\bar{M}n$ 2.17. A colorless product was observed.

EXAMPLE 47

The Use of $Co(II)(DC\text{-}BF_2)_2(H_2O)_2$ as a Catalytic Chain Transfer Agent in the Free Radical Suspension Polymerization of Methyl Methacrylate

The General Procedure for suspension polymerization was followed. The cobalt catalyst was prepared according to the procedures described in Example 43. The concentration of $Co(II)(DC\text{-}BF_2)_2(H_2O)_2$ was 2.5 ppm. The resulting polymer had $\bar{M}n$ 8,080, $\bar{M}w$ 18,300 and $\bar{M}w/\bar{M}n$ 2.26. A colorless product was observed.

COMPARATIVE EXAMPLES 3-6

Attempted Use of $Co(II)(DHIB\text{-}H)_2(H_2O)_2$, $KCo(CN)_5$ and Co(II)Salen as Catalytic Chain Transfer Agents in the Free Radical Emulsion Polymerization of Methyl Methacrylate

[Salen = N,N'-bis(salicylidene)ethylenediamines]

The General Procedure for emulsion polymerization was followed using the indicated type and amount of Co(II) catalyst and hexadecyltrimethylammonium bromide [0.025 M] as the cationic emulsifier. The results are listed below.

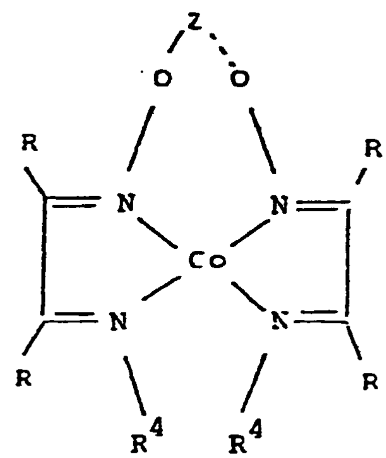
Example	Catalyst	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
3	None	368,000	3,655,000	9.93
4	$Co(II)(DHIB\text{-}H)_2(H_2O)_2$ [50 ppm]	281,000	3,799,000	13.5
5	Co(II)Salen [500 ppm]	372,000	3,794,000	10.2
6	$K_3Co(CN)_5$ [50 ppm]	256,000	3,607,000	14.1

BEST MODE FOR CARRYING OUT THE INVENTION

The best mode presently contemplated for carrying out the invention is represented by the disclosure and claims herein, it being understood that selection of the best mode will depend on a variety of factors, including the monomer(s) being polymerized, the chain transfer agent and the initiator employed, and the amounts thereof, and the polymerization conditions, such as temperature, pressure, conversion and yield.

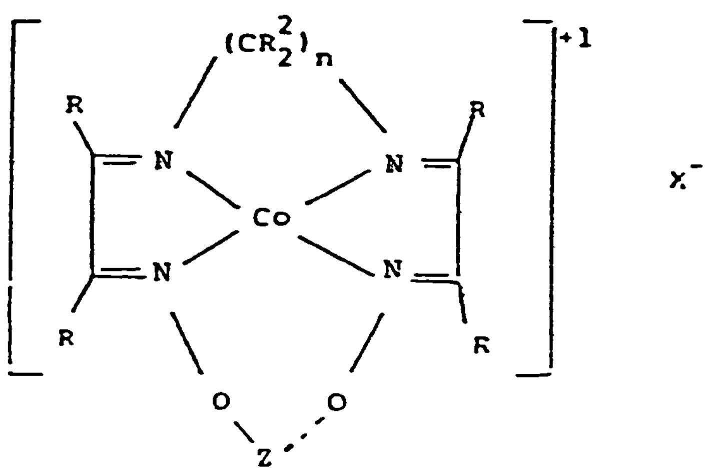
CLAIMS:

1. In an improved free radical bulk, solution, suspension or emulsion polymerization of monomer comprising contacting monomer with initiator, solvent, and suspending or emulsifying agent, as necessary, in the presence of a molecular weight control agent, the improvement characterized in that the molecular weight control agent is a cobalt chelate chain tranfer agent of the formula

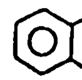
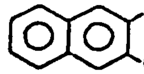


(III)

or



(IV)

wherein each R, independently, is phenyl or C_1 to C_{12} alkyl wherein each α-carbon atom contains two hydrogen atoms, or R and R on adjacent carbon atoms, taken together, is C_5 to C_8 cycloalkylene, unsubstituted in the α-positions, -CH=CH-CH=CH-, CH=CH-, or CH=CH-; R^2 is H or C_xH_{2x+1} wherein x is 1 to 12; each R^4, independently, is H or C_xH_{2x+1} wherein X is 1 to 12, or both R^4 groups taken together is -O-Z---O-; n is 2 or 3; Z is BF_2, BCl_2, BBr_2 or BR^2_2; and X^- is NO_3^-, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, SbF_6^- or R^1COO^- wherein R^1 is C_1 to C_{12} alkyl.

2. Process of Claim 1 which is a bulk or solution polymerization carried out at 50-150°C.

3. Process of Claim 1 which is a suspension or emulsion polymerization carried out at 25-90°C.

4. Process of Claim 1, 2, or 3 wherein the monomer is selected from the group consisting of methacrylate; acrylate; acrylic acid; styrene; vinyl acetate; acrylonitrile; methacrylonitrile; vinyl halides of the formula CH_2=CHX, wherein X is Cl or F; vinylidene halides of the formula CH_2=C(X)$_2$, wherein each X is, independently, Cl or F; substituted butadienes of the formula CH_2=C(R)C(R)=CH_2, wherein each R is, independently, H, C_1 to C_{10} alkyl, Cl or F; ethylenesulfonic acid derivatives of the formula CH_2=$CHSO_3X$, wherein X is Na, K, Li, N(R)$_4$, H, R, or $(CH_2)_nZ$, each R is, independently, C_1 to C_{10} alkyl, n is an integer from 1 to 10, Z is COOY, OH, N(R)$_2$, or SO_3Y, and Y is H, Li, Na, K or N(R)$_4$; acrylamide derivatives of the formula CH_2=CHCON(R)$_2$, wherein each R is, independently, H, C_1 to C_{10} alkyl, or $(CH_2)_nZ$, n is an integer from 1 to 10, Z is COOY, OH, N(R)$_2$, or SO_3Y and Y is H, Li, Na, K, or N(R)$_4$; methacrylamide derivatives of the formula CH_2=C(CH_3)CON(R)$_2$, wherein each R is, independently, H,

C_1 to C_{10} alkyl or $(CH_2)_nZ$, n is an integer from 1 to 10, Z is COOY, OH, $N(R)_2$, SO_3Y, and Y is H, Li, Na, K, or $N(R)_4$; vinyl acetates of the formula CH_2=CHOOCR, wherein R is C_1 to C_{10} alkyl; and mixtures thereof.

5. Process of Claim 1, 2, or 3 wherein the monomer is selected from the group consisting of methyl methacrylate, styrene and methacrylonitrile.

6. Process of any one of Claims 1 to 5 wherein the cobalt chelate chain transfer agent is of formula III.

7. Process of any one of Claims 1 to 6 wherein both R^4 groups taken together is -O-Z---O- and Z is BF_2.

8. Process of any one of Claims 1 to 6 wherein the cobalt chelate chain transfer agent is selected from the group consisting of Co(II)(2,3-dioxyiminobutane-$BF_2)_2$, Co(II)(1,2-dioxyiminocylohexane-$BF_2)_2$ and Co(II)(1,2-diphenyl-1,2-dioxyiminoethane-$BF_2)_2$.

9. Process of any one of Claims 1 to 8 wherein the initiator is selected from the group consisting of azocume, 2,2'-azobis(isobutyronitrile), 2,2'-azobis-(2-methyl)-butanenitrile, 4,4'-azobis(4-cyanovaleric acid), and 2-(t-butylazo)-2-cyanopropane.

10. Process of any one of Claims 1 to 8 wherein the initiator is selected from the group consisting of benzoyl peroxide, lauroyl peroxide, persulfates, and molecular hydrogen.

0199436

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 30 1444

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
D,A	JOURNAL OF POLYMER SCIENCE: POLYMER CHEMISTRY EDITION, vol. 19, 1981, pages 879-889, John Wiley & Sons, Inc., New York, US; N.S. ENIKOLOPYAN et al.: "Catalyzed chain transfer to monomer in free radical polymerization"		C 08 F 2/38

D,A	US-A-4 526 945 (G.M. CARLSON et al.)		

A	US-A-4 169 092 (J.W. BAYER)		

			TECHNICAL FIELDS SEARCHED (Int Cl 4)
			C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-06-1986	CAUWENBERG C.L.M.

CATEGORY OF CITED DOCUMENTS

X particularly relevant if taken alone
Y particularly relevant if combined with another document of the same category
A technological background
O non-written disclosure
P intermediate document

T theory or principle underlying the invention
E earlier patent document, but published on, or after the filing date
D document cited in the application
L document cited for other reasons

& member of the same patent family, corresponding document